I. CRITICAL COMPARISON BETWEEN PRECESSION AND WEISSENBERG METHODS FOR X-RAY SINGLE CRYSTAL STRUCTURAL ANALYSIS

II. X-RAY DIFFRACTION INVESTIGATIONS ON VARIOUS SUGAR DERIVATIVES WITH AN ATTEMPT TO STUDY THE CHEMICAL NATURE OF GLUTOSE

BY

HUNG KAO

B. S., National Central University, China, 1943

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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R. UNIV. BIBLIOTHEEK LEIDEN

PART I

CRITICAL COMPARISON BETWEEN PRECESSION AND WEISSENBERG METHODS FOR X-RAY SINGLE CRYSTAL STRUCTURAL ANALYSIS

Introduction

While the Weissenberg photographs provide distorted projections of the levels of a reciprocal lattice from which the true reciprocal lattice can be reconstructed only after elaborate interpretation, the new Buerger precession method and the well-known deJong-Bouman method give x-ray photographs which are undistorted images of the reciprocal lattice and which easily can be interpreted by inspection only. Since the precession method was only briefly described in Buerger's monograph (1) and so few people are familiar with this newest and most useful technique, a further study of this method in terms of ultimate crystal structure is very desirable.

Although the precession method has some disadvantages, it has many great advantages over the older methods. Moreover, from theoretical point of view, the combined usage of the precession and Weissenberg cameras will provide a much simpler technique than any single method.

The purposes of this investigation were: first, to study the application of the precession method to crystal structural analysis; second, to give a critical comparison and correlation between the precession and two Weissenberg methods in terms of ultimate crystal structural analysis; and third, to devise a simple procedure for crystal structural analysis involving the combination of the two methods which can be used to solve some difficult structural problems.

Experimental

The crystal structure of 2,4-dinitro-phenylhydrazone of benzaldehypde was first studied by the normal-beam Weissenberg method and then by the precession method.

The crystal structure of zinc salicylate was first studied by the equi-inclination Weissenberg method and then by the precession method.

A simplified procedure of x-ray analysis of crystal structure for these two compounds was investigated. This procedure was followed to study the single crystals of zinc benzoate. The applicability of this procedure to study the needle crystals the orientation of which along its crystallographic axes other than needle axis is extraordinary difficult was tested by needle crystals of zinc acid benzoate.

Summary

Buerger's new precession method for single crystal structural analysis has been studied in its fundamental principles and techniques; its comparison with normal-beam and equi-inclination Weissenberg methods.

A new simpler procedure for x-ray analysis of crystal structure has been investigated. This has been shown to be very successful in studying the needle crystals, the study of which by ordinary methods is very difficult.

Determinations were made of crystal habits, densities, lattice constants and probable space-groups of four compounds, for which no previous x-ray and crystallographical data are available.

PART II

X-RAY DIFFRACTION INVESTIGATIONS ON VARIOUS SUGAR DERIVATIVES WITH AN ATTEMPT TO STUDY THE CHEMICAL NATURE OF GLUTOSE

Introduction

For fifty years chemists and sugar technologists have been puzzled by the true chemical nature of glutose. In 1897, Lobry de Bruyn and Aberda van Ekenstein (2) found that when a solution of a fermentable hexose, glucose or better fructose was heated under mildly alkaline conditions, it underwent a transformation to give a new nonfermentable reducing hexose: named "glutose." Glutose has never been isolated in pure form, therefore, none of its specific properties was known. It gave the general reactions characteristic of ketoses and reduced Fehling's solution. The only evidence of its existence was that it formed an osazone melting at 165° C. Without any experimental evidence a 3-keto hexose structure was assigned to it by its discoverers.

Numerous investigators have studied this problem. Although none of the investigators was able to draw any definite conclusions, most of them considered it to be a mixture of several substances.

More recently, definite progress in this field has been made through a series of investigations by Sattler and Zerban of the New York Sugar Trade Laboratory (3). They pointed out that glutose is a mixture of 1,2 fructopyranose anhydride and its dimer together with some other unknown substances. They also postulated that the undetermined material might consist of methylglyoxal as well as other carbonyl compounds resulting from the decomposition of fructose solution or from yeast fermentation. This was not confirmed by any experimental evidence.

The chief difficulty which prevents the complete solution of this problem is the fact that there has been no method by means of which minute amount of carbonyl derivatives could be unequivocally identified. The identification of carbonyl derivatives by means of x-ray diffraction patterns by Clark, Kaye and Parks (4) has suggested a new approach to this problem because the sample necessary for identification by this method is ordinarily of the order of 0.5 mg.

Furthermore, the reliability of the melting points of the sugar derivatives is questionable. The osazone of galactose, for instance, is reported with a melting point range of almost twenty degrees in the literature. In the sugar field, the melting points of osazones are not reliable constants by means of which positive identification can be made.

The purposes of this investigation were: (1) to study the x-ray diffraction patterns of various carbonyl compounds related to sugars, with the idea of finding out a unique method for the identification of minute quantities of these derivatives, and (2) to attack the age-old problem of the nature of glutose by means of the x-ray identification method developed in (1).

Experimental

X-Ray powder patterns of the derivatives prepared from the carbonyl compounds such as methylglyoxal, acetomethylcarbinol, hydroxymethylfurfuraldehyde, acetol, diacetyl, etc., and three reagents, namely, phenylhydrazone, 3,5-dinitrobenzoyl hydrazide, diphenylacetohydrazide, were taken with a Hayes powder camera with an effective radius of 7.00 cm. Filtered Cu radiation was used throughout the experiment. The x-ray unit was operated at 40 Kv. 15 ma. Eastman non-screen x-ray films were used. The patterns thus obtained were microphotometered with the Leeds & Northrup recording instrument. In the case of osazone series, the relative intensities and "d" values of each pattern were checked from the determinations by using Norelco Geiger-

Counter x-ray spectrometer. In the other two series the values obtained from the microphotometer were checked by the values obtained from measurements by means of the ordinary G. E. film scale.

Summary

By comparison of the x-ray diffraction patterns of the 3,5-dinitrobenzoyl hydrazone of the known carbonyl compounds and the unknown obtained from the levulose material the presence of methylglyoxal as one of the constituents of the glutose has been definitely proved. The other constituent of the glutose was found to be acetoin.

The identification of the minute amounts of the derivatives of carbonyl compounds by means of their x-ray diffrcation patterns has shown to be eminently successful. In fact, this is the only way to identify these compounds unequivocally when only a trace of the material is available.

X-Ray diffraction patterns of the osazones, 3,5-dinitrobenzoylhydrazones, and diphenylacetohydrazones of several carbonyl compounds have been studied. The "d" values and the relative intensities of the diffraction lines of each pattern have been determined.

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VITA

The author was born May 29, 1919, in King-Yang, Shensi, China, and received his primary educations there. After the death of his widow mother, he was then brought up by his uncle, Mr. Kao Lan-Ting, through whose assistance he was able to carry on his education through "middle" schools, college and finally to come over to the Graduate School of the University of Illinois. After the graduation from the National Central University, Chungking, China, in June, 1943, with the degree of Bachelor of Science, he held an assistantship in the Department of Chemistry of the same University until November, 1944, when he started his trip to United States.

He entered the Graduate School of the University of Illinois in February, 1945. During this time he held a fellowship of the University of Illinois from June, 1946, to September, 1947. His engagement to Miss P. S. Lee was announced in October, 1943.

He is a member of the following organizations: The American Chemical Society, The American Association for the Advance of Science ,Sigma Xi, and Phi Lambda Upsilon.